

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT
 (PCT Article 36 and Rule 70)

Applicant's or agent's file reference V80037WO	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/CA 03/01520	International filing date (day/month/year) 03.10.2003	Priority date (day/month/year) 03.10.2002
International Patent Classification (IPC) or both national classification and IPC C23C18/02		
Applicant ALBERTA RESEARCH COUNCIL INC. et al.		



- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 9 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 11 sheets.

- This report contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/CA 03/01520

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-4, 7-12, 15, 17	as originally filed
5, 6, 13, 14, 16, 18, 19	received on 26.08.2004 with letter of 25.08.2004

Claims, Numbers

1-6, 7 (part), 42 (part)	as originally filed
7 (part), 8-41, 42 (part)	received on 26.08.2004 with letter of 25.08.2004

Drawings, Sheets

1/4-4/4	as originally filed
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2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)):
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

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5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	4,8-40,42
	No: Claims	1,2,3,5,6,7,41
Inventive step (IS)	Yes: Claims	10-25
	No: Claims	4,8,9,26-40,42
Industrial applicability (IA)	Yes: Claims	1 - 42
	No: Claims	

2. Citations and explanations

see separate sheet

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Re Item I

Basis of the report

The amendments made in claims 10 and 26 do not meet the requirements of Article 34(2)(b) PCT, because no basis can be found in the original disclosure.

There is no statement in the original disclosure that the method step a) of claim 10 has to exclude a sol. There is also no teaching that the sol, modifier agent and filler particles all together are selected to avoid gelation of the sol. This teaching is also not implied for the skilled person.

For the preparation of the International preliminary examination report therefore the originally filed claims 10 and 26 will be the basis.

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Reference is made to the following documents:

- D1: US-A-5 711 987 (BEARINGER CLAYTON R ET AL) 27 January 1998 (1998-01-27)
- D2: EP-A-1 069 074 (N T S CORP ;RYOWA CORP (JP)) 17 January 2001 (2001-01-17)
- D3: US-A-5 626 923 (FITZGIBBONS JERRY M ET AL) 6 May 1997 (1997-05-06)
cited in the application
- D4: US-A-5 710 203 (CAMILLETTI ROBERT CHARLES ET AL) 20 January 1998
(1998-01-20)
- D5: US-A-4 931 413 (WEIR RICHARD L ET AL) 5 June 1990 (1990-06-05)
- D6: DE 39 28 845 A (BOEHLER AG) 7 March 1991 (1991-03-07)

2. Novelty (Article 33(2) PCT).

2.1. D1 discloses a protective coating for electronic devices, such as chips, which consists of at least two layers. The first layer comprises a preceramic silicon containing material

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and at least one filler. The second layer is a resin sealer coat made from a colloidal inorganic siloxane resin or an organic resin, such as a polyimide (abstract). More specifically, the preceramic silicon containing material of the first layer is a precursor to silicon oxides, which either comprise a hydrolysed or partially hydrolysed material (col. 2, line 53 - 67), which may contain a dispersion of colloidal silica (col. 4, line 19 - 28), or a hydrogen silsesquioxane. The silica particles in colloidal silica are considered to be vitreous, since they do not have an ordered crystalline structure but are also not fully amorphous.

Hence, D1 discloses a coating comprising vitreous particles, a filler and the solid content of a ceramic liquid precursor.

Fillers are listed in col. 5 and 6 and comprise, for example, SiC, AlN, Al₂O₃, SiO₂. In case of SiO₂ the average particle size is between 5 - 40 µm. The preferred filler is a mixture of WC, W metal, diamond dust and P₂O₅ (col. 6, line 61 - 63, and col. 10, line 54 - 62).

The constituents of the coating are preferably mixed into a dispersion and applied by common wet coating processes (col. 7, line 24 - 55), followed by curing at temperatures between 50 - 1000°C, more preferably between 50 - 800°C and most preferably between 50 - 450°C (col. 7, line 56, - col. 8, line 12). The sealing preferably is made by application of a colloidal siloxane resin (col. 8, line 25 - 47), e.g. by dipping, and cured between 60 - 400°C, more preferably between 350 - 400°C (col. 9, line 39 - 46).

Hence, claims 1, 2, 3 and 7 lack novelty in view of D1.

2.2. D2 teaches compositions for the formation of protective coatings based on hydrotalcite (abstract). In one embodiment the hydrotalcite is mixed with TiO₂ fine particles and colloidal silica as the binder. Colloidal silica is considered to be vitreous. In addition to TiO₂ further inorganic compounds may be added with a mean particle size of 1 µm or smaller, including silica and other silicon oxides ([0036] and [0037]). The mixture is set up as a slurry ([0017] - [0021]). Additions of water and alcohol serve to adjust the pH. Heating of the coatings after their application, at least to remove the solvent, is implied.

However, there is no coating taught, which comprises vitreous particles and the solid content of a ceramic liquid precursor and a filler.

Hence, claims 1 - 42 are novel over D2.

2.3. D3, which was cited by the Applicant, discloses a method for providing a ceramic coating on a ceramic or a metallic substrate (abstract). In example 1 a dispersion of YSZ, Al₂O₃, a glass-ceramic filler and SiO₂ (IPA-ST from Nissan chemicals) is prepared in

isopropanol. Since the SiO_2 in IPA-ST has nanoscale dimensions it must be assumed that the commercial product is a sol. To this dispersion KOH is added, which results in gelling. In a next step the gel is applied to an Inconel sheet.

Analogous coatings are prepared in examples 2 and 3, which even mention use of a SiO_2 sol. Hence, D3 produces coatings which comprise the same combination of technical features as claims 1, 2, 3, 5 and 6. A coating does not necessarily be novel if being produced by a novel process.

Method claim 10 is novel, because D3 does not teach to apply a sol to a coating of a filler and vitreous particles. Method claim 26 is novel, because D3 does not reveal to add an agent to prevent gelling (in fact, it is on purpose in D3 to gel the composition before applying it to a metal sheet).

2.4. D4 teaches coatings for electronic devices (abstract). In example 3 a coating composition is disclosed consisting of silica glass microballoons (see also example 1), alumina, a silsesquioxane, a silane and a decane. After application of the composition to an Al panel it is heated at 185°C and at 400°C . D4 further contemplates to apply a further coating to the first coating (col. 5, line 66, - col. 6, line 15).

Hence, claims 1, 6, 7 and 41 lack novelty over D4. Method claim 10 is novel, because D4 does not teach to apply a sol to a coating of a filler and vitreous particles.

Claim 26 is novel over D4, because D4 does not disclose to add a pH modifier to the coating preparation to prevent gelation.

3. Inventive step (Article 33(3) PCT).

3.1. Claim 4 is not considered inventive, because the boro-silicate glass mentioned in this claim is considered as a mere variation of the glass particles used in D3 not involving any non-obvious technical effects.

3.2. Claims 8 and 9 are not inventive. Sealing of ceramic coatings prepared from compositions of fillers, vitreous particles and sols is already known from D1 and D4. Use of silica sols for sealing is known in the art (D5, abstract and col. 3, line 66, - col 4, line 23, and D6, abstract and col. 4, line 13 - 30). Use of polyimide is already disclosed in D1 (col. 8, line 13 - 16). Claim 42 is a mere juxtaposition of an inorganic and an organic sealing, which does not provide any unexpected effects.

3.3. Even without the teachings of D1 and D4, independent claim 7 would not be inventive, because sealing of porous ceramic coatings in general is known in the art (D5, D6) and the skilled person will always consider such a sealing if problems arise related to porosity (permeability for corrosives, strength of the coating, etc.).

3.4. Claim 26 is not inventive. D1, D3 and D4 disclose sol compositions comprising vitreous particles and a filler for coating of substrates. It is common knowledge that sols can form a gel, if the pH value, concentration or polarity of the solvent are not chosen properly. Hence, the skilled person seeking to keep the sol stable would choose these parameters accordingly, which also involves to add a pH modifier agent. Note that the definition of the heating conditions in step d) is vague (see item VIII, *infra*).

3.5. Claims 27 - 40 are not considered to be inventive. The additional subject-matter of these claims is either already disclosed in D1 - D4 or can be determined by the skilled person by due experimentation (like temperatures).

3.6. Subject-matter of independent claim 10 is considered inventive.

As the objective problem with respect to D1, D3 and D4 it is seen to provide a wet ceramic coating method, which has less shrinkage than the methods of these documents and thereby results in less defects and debonding of the coating.

This problem is solved by the method of claim 10 in which the coating is generated successively, i.e. first, a coating of the vitreous particles and the filler is applied to the substrate and heated, and, second, a ceramic sol is applied and the coating heated again. Such an approach is not derivable by combination of any of the documents of the search report. In addition, these documents do not hint how the problem of shrinkage of the coated film during its preparation could be assessed.

Consequently, also claims 11 - 25 are considered inventive.

4. Industrial applicability (Article 33(4) PCT).

Claims 1 - 42 fulfill the requirement of industrial applicability, since subject-matter of present application can be made or used (in a technological sense) in industry (Article 33(4) PCT).

Re Item VII

Certain defects in the international application

The application does not comply with the provisions of Rule 5.1.a.ii PCT, because the most relevant prior art, e.g. documents D1, D3 and D4, has not been cited or briefly discussed.

Re Item VIII

Certain observations on the international application

Clarity

1. Claims 1 - 9, 41 and 42 refer to a ceramic coating per se. However, such a coating only exists in combination with a substrate, because it is assumed that after its application of the precursor material to a substrate the resulting coating cannot be removed anymore without losing its coating properties.

2. The following claims are defined by the result to be achieved (desiderata claims) instead of by definition of technical features which, in combination with the known combination of technical features, would provide these results. A definition of claimed subject-matter by the result to be achieved is only allowable in exceptional cases (see PCT Gazette, section IV, paragraph III-4.7).

Claim 10, steps c) and e): "... heating until the coating has sufficient integrity ...", "... heating under conditions sufficient to cause ...".

Claim 11: "... heated under conditions sufficient to provide ...".

Claims 15 and 28: "... conditions sufficient to sinter ...".

Claims 21 and 37: "... temperature sufficient to bond ...".

Claim 26, steps a) and d): "... a sufficient amount ..." and "heating the coating under conditions sufficient to cause an interaction between the fine vitreous particles and the solid component ...".

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3. Article 5 PCT in conjunction with PCT Gazette 10/98, section IV, II-4.16, requires use of trademark signs for commercially available products. However, on pages 13 and 14 some of the commercially available products lack these signs.

4. Statements, like on page 19, line 22 - 24, which try to expand the matter for which protection is sought as lying within the "spirit and scope of the invention" render the definition of the subject-matter of the claims unclear (Article 6 PCT).

According to another aspect of the invention, there is provided a method of forming a composite coating that first involves forming a ceramic coating as described above, then applying a sealant onto the ceramic coating, such that the sealant penetrates at least the surface layer of the coating, then,
 5 heating the coating at a temperature sufficient to bond the sealant to the ceramic matrix. The sealant may be in liquid form and if so, may be applied to the coating by one of dip-coating or spraying. Alternatively, the sealant may be applied to the coating by one of powder coating, spray-coating, dip-coating, and spin-coating.

10 According to another aspect of the invention, there is provided another method of producing a protective ceramic coating and applying the coating onto a substrate. In this method a preparation is formed by mixing together a ceramic sol, a liquid carrier, a sufficient amount of pH modifier agent to prevent gelation of the sol, and filler particles selected from the group of
 15 ceramic, glass, and metal particles. Then, fine vitreous particles are mixed into the preparation, Then, the preparation is applied onto a substrate to form a coating on the substrate. Then, the coating is heated under conditions sufficient to cause an interaction between the fine vitreous particles and the solid component of the ceramic sol, thereby forming a ceramic matrix with
 20 filler particles integrated therein.

The coating may be heated at between 550-850°C. More particularly, the coating may be heated at between 650-850°C under conditions sufficient to sinter the coating.

25 The preparation may be applied to the substrate by spin-coating. Or, the coating may be applied by one of spraying or dip-coating, in which case, additional liquid carrier is first applied to the preparation to dilute the preparation, before spraying or dip-coating.

A sealant may be applied onto the coating such that the sealant penetrates at least the surface layer of the coating. Then, the coating is
 30 heated at a temperature sufficient to bond the sealant to the ceramic matrix. The sealant may be in solution form and be applied to the coating by one of

dip-coating or spraying. Alternatively, the sealant may be applied to the coating by one of powder coating, spray-coating, dip-coating, and spin-coating.

5 Brief Description of the Drawings

Figure 1 is a flowchart illustrating one method of producing a ceramic coating wherein a ceramic sol is mixed in a separate step with glass and filler particles.

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Figure 2 is a flowchart illustrating another method for producing a ceramic coating wherein a ceramic sol and glass particles are mixed in a single step.

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Figure 3 is a Scanning Electron Microscopy (SEM) image of a pair of metal substrates coated with a protective ceramic coating.

Figure 4 is a Scanning Electron Microscopy (SEM) image of a composite polymer-ceramic protective coating on a substrate.

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Detailed Description of Embodiments of the Invention

Each of the embodiments of the invention described herein relate to a protective ceramic-containing coating, and a method of preparing the coating and applying it on substrates made of various materials, including metal, glass and ceramic. Generally speaking, a coating preparation is prepared by mixing materials that include filler particles, fine vitreous particles such as glass, a ceramic liquid such as a ceramic sol, and in some cases, a liquid carrier. Then, the preparation is deposited on the substrate by a suitable technique that includes spin-coating, dip-coating, spray-coating, painting or screen-printing. The coated substrate is then dried to remove the liquid component of the coating, and a sintering step is applied to fully develop a ceramic matrix in situ in the coating; that is, the coating is sintered at a sustained elevated temperature to cause solid particles of the ceramic sol precursor to interact

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Example A: Base Coating 1 (BC1)

A coating slurry was prepared by method P1 by mixing 63g of Alcan C94 alumina, 23.8g Alcoa A16SGD alumina and 14g Tosoh TZ-8Y zirconia as fillers with 6.25g Glass 1 in 300ml of water and 100ml of isopropanol.

- 5 Also, 40 ml of solution 5wt% of Polyox® in water was used as the water soluble polymer. The slurry was ball-milled for 4 hours, and then sprayed on an Inconel 625 substrate, and presintered at 560°C for 0.5 hours. After cooling to ambient temperature, the deposit was top-coated with a 0.5M Alumina ceramic sol in five dip-coating/drying cycles and sintered at 750°C for 0.5
- 10 hours. The resulting base coating was examined and found to be porous, crack-free and had an average thickness of 35µm.

Example B: Base Coating 2 (BC2)

- A coating slurry was prepared by method P1 by mixing 10g of Alcan C94 alumina, 40 g aluminum powder with average particle size of 5µm, 10g of
- 15 UK Abrasives F1500 boron carbide powder, 23.8g Alcoa A16SGD alumina and 14g Tosoh TZ-8Y zirconia as fillers with 6.25g Glass 3 in 300ml of water and 100ml of isopropanol. A water soluble polymer was used comprising 40 ml of solution 5wt% of Polyox® in water. The slurry was ball milled for 4 hours
- 20 then sprayed on an Inconel 625 substrate, and pre-sintered at 600°C. After cooling, the ceramic deposit was top coated with a 0.1 M zirconia ceramic sol in four dip-coating/drying cycles and sintered at 800°C for 0.5 hours.

- The resulting base coating was examined and found to be crack-free
- 25 and have an average thickness of 30 µm. Microscopic observation showed that both aluminum and B₄C components showed a certain degree of oxidation. If avoiding oxidation of metallic or non oxide fillers is desired, the sintering can be conducted in protected atmosphere (such as Nitrogen, Argon etc.)

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Example C: Base Coating 3 (BC3)

A coating preparation was prepared according to method P2 by mixing 93g of Alcoa A300FI alumina and 93g Alcoa A16SGD as fillers and 310ml of isopropanol. A ceramic precursor matrix component of 10ml of DuPont Ludox HS-40 ceramic sol was added directly to the preparation. For pH correction and in order to prevent the gelation of the sol, 20ml of 2wt% solution of ammonia in water was also added. The preparation was ball-milled for 4 hours and 62.5g Glass 1 in 310ml of water was added. No water soluble polymer addition or dispersant was used. The preparation was then ball milled for about 10 hours. Then, the preparation was applied on a stainless steel 316 substrate by spin coating and sintered at 710°C for 0.5 hours.

Upon examining the coated substrate, it was observed that the resulting coating had a multitude of vertical micro-cracks and an average thickness of 200µm. Such vertical micro-cracks in coating are expected to contribute some thermal stress resistance and an increased adhesion of the coating to the substrate.

Example D: Base Coating 4 (BC4)

A coating preparation was prepared using method P2 by mixing 93g of Alcoa A300FI alumina and 93g Alcoa A16SGD as fillers and 310ml of isopropanol. A ceramic precursor matrix component of 10ml of DuPont Ludox HS-40 ceramic sol was added directly to the preparation. For pH correction and in order to prevent the gelation of the sol, 20ml of 2 wt% solution of ammonia in water was added to the preparation. No water soluble polymer addition was used. Optionally, dispersants may be added at this stage. The preparation was ball milled for about 4 hours then 62.5 g of Glass 1 was added. Then, the preparation was ball milled again for about another 10 hours. Then, an additional 310ml of water and 310ml of isopropanol were added and the resulting preparation was ball milled for about 4 hours then applied on a carbon steel 4130 substrate by spraying. The coating was then sintered at 680°C for about 0.5 hours.

A proper quality zirconia silica solvent base sol should be a clear yellow transparent liquid.

5 To the liquid component prepared as described above, a mixture of 58g of Alcoa A3000FI alumina and 58g Alcoa A16SGD as fillers and 36 g of Glass 1 was added and the resulting suspension was subjected to vibromilling for 4 hours, then was applied on a carbon steel 4130 substrate by spraying. The coating was then sintered at 680°C for about 0.5 hours.

10 The resulting base coating was observed to be smooth with very few micro-cracks and had an average thickness of 50µm.

According to another embodiment of the invention, the ceramic coating
15 may be infiltrated by a sealant to form a composite sealant-ceramic coating that provides additional protective properties over the ceramic-only coating. Such sealant includes inorganic sealants and organic sealants.

The inorganic sealing process for forming the composite coating
20 involves first applying a solution of inorganic solution over a ceramic coating prepared by one of methods P1 and P2. Suitable inorganic sealants include water soluble ceramic precursors such as solutions of sodium borate, boric acid, and mixed borophosphates or mixtures of ceramic sols and silica sol sodium borate, boric acid, and mixed borophosphates. The preferred
25 methods of application of the inorganic sealant solution are dip-coating or spraying. The sealant solution penetrates the ceramic coating by entering through the open pores of the ceramic coating. Sufficient sealant is applied to provide a homogeneous penetration of the open pores beyond the surface layer. Then, a thermal treatment is applied at a temperature up to the
30 sintering temperature of the base ceramic coating. For example, a suitable thermal treatment is heating at 470-800°C for 30 minutes for simple shape parts. After sintering, mechanical bonding (at least interlocking) was found within most of the coatings between the sealant and the matrix particles.

penetrated ceramic coating was then dried. Then, the coating was subjected to a heat treatment step at 600°C for 30 minutes. The sealing treatment resulted in a fully dense composite coating having a 400Hv measured hardness.

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Example G: Inorganic Sealant / Ceramic Composite Coating 2

Base coating BC1 was subjected to consecutive cycles of sealant penetration by dip-coating the base coating BC1 five times in a mixture of 5 wt% solution of sodium aluminum borophosphate. The penetrated coating was then dried and then cured at 470°C. The sealing treatment resulted in a porous ceramic coating with a 270 Hv hardness.

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Example H: Inorganic Sealant / Ceramic Composite Coating 1

Base coating BC3 was subjected to 4 consecutive cycles of penetration by dip coating with a mix of 100 ml DuPont Ludox TMA, 100ml of distilled water and 9.5g boric acid and drying. The penetrated coating was then dried and then cured at 710°C for 30 minutes. The sealing treatment resulted in a porous ceramic coating with a 210 Hv hardness.

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The following examples are experiments involving producing a composite coating comprising a base ceramic coating penetrated with an organic polymer sealant:

Example I: Organic Sealant / Ceramic Composite Coating 1

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The inorganic sealant / ceramic composite coating produced in Example G was subjected to consecutive cycles of sealant penetration by dip-coating the base coating in a 5wt% solution of Polyether Sulfone in N-Methyl Pyrolydone. The penetrated coating was then dried and then subjected to a heat treatment for 30 minutes at 300°C. The resulting composite coating was found to be fully sealed.

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Example J: Organic Sealant / Ceramic Composite Coating 2

The surface of the inorganic sealant / ceramic composite coating produced in example I was sprayed with a 10 μ m layer commercial polymer coating system (DuPont 958207) containing a mixture of FEP and Polyimide. The coating was then cured at 340°C for 30 minutes, which melted the FEP, thereby enabling the polymer to penetrate the pores of the ceramic coating. The resulting sealant / ceramic composite coating was found to be completely sealed.

Example K: Organic Sealant / Ceramic Composite Coating 3

The surface of the base coating BC4 was top-coated with a layer of agglomerated FEP particles by an electrostatic powder coating method as known in the art. The coating was then cured at 340°C for 30 minutes, which melted the FEP, thereby enabling the polymer to penetrate the pores of the ceramic coating. The resulting sealant / ceramic composite coating was found to be completely sealed. Figure 4 shows a SEM cross-section view of this composite coating. On the top of the composite ceramic-polymer coating, a layer of excess polymer phase is observable. The composite coating consists of a mix of two continuous matrices of ceramic and polymer materials, the porous ceramic matrix being completely penetrated by a continuous polymer phase.

While the preferred embodiment of the invention has been illustrated and described, it will be appreciated that various changes can be made therein without departing from the scope and spirit of the invention.

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- (b) a sealant penetrating at least the surface layer of the ceramic coating.
8. The coating of claim 7 wherein the sealant is an inorganic material derived from a liquid ceramic precursor, the ceramic precursor being selected from the group of sodium borate, boric acid, mixed borophosphates, and, mixtures of ceramic sols and silica sols sodium borate, boric acid, and mixed borophosphates.
9. The coating of claim 7 wherein the sealant is an organic polymer containing at least one resin selected from the group of polytetrafluoroethylene, tetrafluoroethylene-perfluorovinyl ethers copolymers, fluorinated ethylene-propylene copolymers, low density polyethylene, poly ether sulfone, polyimide, and epoxy resins.
10. A method of producing a protective ceramic coating and applying the coating onto a substrate, the method comprising:
- (a) forming a preparation by mixing together fine vitreous particles, a liquid carrier, and filler particles selected from the group of ceramic, glass, and metal particles;
- (b) applying the preparation onto a substrate to form a coating on the substrate;
- (c) heating the coating until the coating has sufficient integrity to be coated with a ceramic sol;
- (d) applying a ceramic sol onto the coating such that the sol penetrates the pores of the coating; then
- (e) heating the coating under conditions sufficient to cause an interaction between the fine vitreous particles and the solid component of the ceramic sol, thereby forming a ceramic matrix with filler particles integrated therein.

and from the group of metallic particles consisting of aluminum, stainless steel, and nickel alloys.

21. The method of claim 10 further comprising after step (e), applying a sealant onto the coating such that the sealant penetrates at least the surface layer of the coating, then, heating the coating at a temperature sufficient to bond the sealant to the ceramic matrix.
22. The method of claim 21 wherein the sealant is in solution form and is applied to the coating by one of dip-coating or spraying.
23. The method of claim 21 wherein the sealant is applied to the coating by one of powder coating, spray-coating, dip-coating, and spin-coating.
24. The method of claim 22 wherein the sealant is an inorganic material derived from a liquid ceramic precursor, the ceramic precursor being selected from the group of sodium borate, boric acid, mixed borophosphates, and, mixtures of ceramic sols and silica sols sodium borate, boric acid, and mixed borophosphates.
25. The method of claim 23 wherein the sealant is an organic polymer selected from the group of polytetrafluoroethylene, tetrafluoroethylene-perfluorovinyl ethers copolymers, fluorinated ethylene-propylene copolymers, low density polyethylene, poly ether sulfone, polyimide, and epoxy resins.
26. A method of producing a protective ceramic coating and applying the coating onto a substrate, the method comprising:
 - (a) forming a preparation by mixing together a ceramic sol, a sufficient amount of pH modifier agent to prevent gelation of the sol, and filler particles selected from the group of ceramic, glass, and metal particles;
 - (b) mixing in fine vitreous particles to the preparation;

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- 5
- (c) applying the preparation onto a substrate to form a coating on the substrate;
- (d) heating the coating under conditions sufficient to cause an interaction between the fine vitreous particles and the solid component of the ceramic sol, thereby forming a ceramic matrix with filler particles integrated therein.
- 10
27. The method of claim 26 wherein the coating is heated at between 550-850°C.
28. The method of claim 27 wherein the coating is heated at between 650-850°C under conditions sufficient to sinter the coating.
- 15
29. The method of claim 26 wherein the fine vitreous particles are glass particles having an average particle size of 5 μm or less.
30. The method of claim 29 wherein the glass particles of the matrix are selected from the group of lithium sodium borosilicate glass, and glasses containing SiO_2 , Al_2O_3 , B_2O_3 , P_2O_3 , ZrO_2 , and TiO_2 .
- 20
31. The method of claim 30 wherein the fine glass particles are lithium sodium borosilicate glass that includes up to 10 wt. % additive oxides selected from the group of Fe, Ni, Co, V, Sb, P, and Mn.
32. The method of claim 26 wherein the ceramic sol is selected from the group of ceramic sols of alumina, silica, titania, and zirconia.
- 25
33. The method of claim 26 wherein the filler material is selected from the group of ceramic particles consisting of alumina, silica, titania, magnesia spinel, B_4C , BN, SiC, AlN, Sialon, and mixtures thereof, and from the group of metallic particles consisting of aluminum, stainless steel, and nickel alloys.
34. The method of claim 26 wherein in step (c), the preparation is applied to the substrate by spin-coating.

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35. The method of claim 26 further comprising in step (a), adding a liquid carrier to the preparation.
- 5 36. The method of claim 26 wherein between steps (b) and (c), a liquid carrier is applied to the preparation to dilute the preparation, then in step (c), the preparation is applied to the substrate by one of spraying or dip-coating.
- 10 37. The method of claim 26 further comprising after step (d), applying a sealant onto the coating such that the sealant penetrates at least the surface layer of the coating, then, heating the coating at a temperature sufficient to bond the sealant to the ceramic matrix.
- 15 38. The method of claim 37 wherein the sealant is applied to the coating by one of powder coating, spray-coating, dip-coating, and spin-coating.
39. The method of claim 37 wherein the sealant is an inorganic material derived from a liquid ceramic precursor, the ceramic precursor being selected from the group of sodium borate, boric acid, mixed borophosphates, and, mixtures of ceramic sols, sodium borate, boric acid, and mixed borophosphates.
- 20 40. The method of claim 38 wherein the sealant is an organic polymer selected from the group of polytetrafluoroethylene (PTFE), tetrafluoroethylene-perfluorovinyl ethers copolymers, fluorinated ethylene-propylene copolymers, low density polyethylene, poly ether sulfone, polyimide, and epoxy resins.
- 25 41. The coating of claim 1 wherein the solid content of the ceramic liquid precursor is a solid component of a ceramic sol.
42. The coating of claim 7 wherein the sealant comprises:
- (a) an inorganic material derived from a liquid ceramic precursor, the ceramic precursor being selected from the group of sodium borate, boric acid, mixed borophosphates, and, mixtures of